Electronic Spectroscopy as a Probe for the Mechanism of a Chromium(II) Catalysed Substitution Reaction

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Experiment Overview

The activities involved in this experiment are:

- Prepare and/or collect of solution state spectra of a series of homoleptic complexes of chromium(III) so as to arrive at an experimentally-based spectrochemical series.
- Collection of the solid state UV-Vis spectra of $CrCl_3$ (anhydrous) and $KCr(SO_4)_2.12H_2O$ so as to determine (using the rule of average environment) the coordination environment of chromium(III) in the salt $CrCl_3.6H_2O$.
- Establish the connection between the solution and solid state spectra and use this to confirm that over a short timescale the coordination sphere of chromium(III) in $CrCl_3.6H_2O$ does not change on dissolution. This conclusion is confirmed by quantitative determination (potentiometric titration) of the concentration of free chloride obtained following dissolution of the salt.
- Determine the relative rates of the first and second aquation reactions of $[CrCl_2(OH_2)_4]^+$
- Record the UV-Vis spectra of the product(s) formed from the chromium(II) catalysed dissolution of anhydrous chromic chloride and use the rule of average environment to deduce (1) whether a single or several products are formed during the reaction and (2) identify the coordination environment of the chromium(III) product. The conclusions drawn from this part of the experiment are used to deduce the path of the catalytic reaction.

Level of Experiment

Third year undergraduate level for students in inorganic chemistry

Keyword Descriptions of the Experiment

Domain
inorganic chemistry

Specific Descriptors
electronic spectroscopy, coordination chemistry, spectrochemical series, substitution reactions, inner-sphere electron transfer, reactivity of transition metal compounds

Course Context

First/second year background:

Students will have encountered the spectrochemical series during the first and second years of their course and will be familiar with the inert / labile categorisation of the transition metals in their different oxidation states from their second-year chemistry course. While students will be aware that the colours of transition metal compounds are the result of excitation of electrons from lower to higher energy d orbitals a more formal description of the electronic structure of transition metals is not dealt with until the third year of their course.

Third year lecture course (running in parallel with the laboratory course) includes:

- An elementary discussion of the electronic structure of transition metal complexes including the basis of Tanabe-Sugano diagrams and interpretation of spectra.
- Description of the dynamics of transition metal compounds.
- Outline of the inner- and outer-sphere mechanisms of electron transfer - the enormous difference in reactivity of $Co^{II/III}$ and $Cr^{II/III}$ is central to that discussion.

The selection of experiments in the laboratory course is not preordained. In any week a maximum of eight students can elect to perform this experiment. Since the laboratory course commences in the first week of semester only a small group of students will have attended all the relevant lectures prior to starting this experiment.

Prerequisite Knowledge and Skills

Knowledge and skill requirements here:

- Basic coordination chemistry (coordination numbers/geometry)
- d-orbital splitting diagram for octahedral complexes
- Coordination environment of Cr^{III} in chrome alum and in anhydrous chromic chloride (prelab)
- Rates of substitution of $Cr^{II/III}$ complexes (prelab)
- Application of the rule of average environment (prelab)

Time Required to Complete

Prior to Lab: 30 min
In Laboratory: 3 h (note - this refers to the ACELL version, where tasks are shared by a pair of students)
After Laboratory: 1 h

Experiment History

The experiment has developed from study of stepwise hydration of hydrated chromic chloride that had run at University College London through the 1980's. While the source of the original experiment is unknown (to SPB) contributions by Professors M.L. Tobe and A.G. Deeming are gratefully acknowledged.